

Fabrication and Crystallization Behavior of BNN Thin Films by H-MOD Process

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Abstract

$Ba_2NaNb_5O_{15}$, hereafter BNN, thin films are attractive candidates for nonvolatile memory and electro-optic devices. In the present work, thin films that have different contents of Ba, Nb and Na have been prepared by H-MOD technique on silicon and Pt substrates. XRD and SEM were used to investigate the phase evolution behavior and the microstructure of the films. It was found that the films of about 500nm thick were crack-free and uniform in microstructure. Nb content strongly influenced the phase formation of the films, where unwanted phases were always formed at the stoichiometric BNN composition. However, the unwanted phases decreased with the increase of excess Nb content, and the single phase (tetragonal tungsten bronze structure) BNN thin film was obtained when the niobium content reached some point. From this study, the sub-solidus phase diagram below 850°C for BaO-Na₂O-Nb₂O₅ ternary system is proposed.

Key Words: BNN; H-HOD; tetragonal tungsten bronze

1. Introduction

Barium sodium niobate $Ba_2NaNb_5O_{15}$ (BNN) is a ferroelectric solid solution compound with well-known tungsten-bronze-type (TTB) structure, which belongs to the point group of $mm2$ at room temperature [1]. BNN has large nonlinear optical coefficients and electro-optic properties. Therefore, BNN has been receiving great attention for application in electro-optic devices [2,3]. In addition, BNN crystals show remarkable polarization of $401 \mu Ccm^{-2}$ and spontaneous of 51 parallel to c axis and suffer no optical damage to an intense laser beam in comparison with $LiNbO_3$.

However, industrial applications of BNN have not been made because the production of single crystals and thin films with sufficient crystalline quality has not yet been successful. The main reason is the occurrence of cracks. The cracking is due to the large thermal expansion of the c -axis at Curie temperature ($\sim 570^\circ C$) during

cooling process [4].

The structure and oxygen octahedral are shown in Figure 1. There are three types of sites (A_1 , A_2 and C). The C sites of BNN are empty, A_1 sites and A_2 sites are filled with Ba^{2+} and Na^+ ions [5].

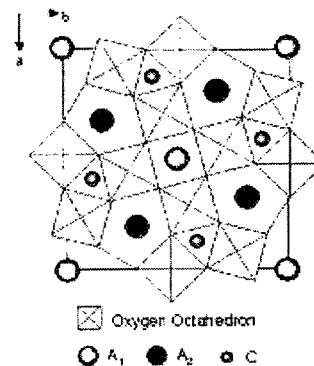


Fig.1. BNN structure showing the three kinds of sites.

That BNN thin films have been prepared in many methods has been reported [6,7]. In this

paper, BNN thin films were prepared by a hybrid metal-organic deposition (H-MOD) process. In this process, metal alkoxides are combined with metal-organic precursors, which are less sensitive to moisture [8]. It retains MODs advantages regarding ease of preparation, insensitivity to water as well as sol-gels advantage of greater oxide thickness per layer of deposition solution. The solution of H-MOD is more stable than sol-gel solution.

In this paper, the effect of composition and annealing temperature on crystallization behavior and microstructure of H-MOD derived BNN thin films is discussed.

2. Experiment procedure

Figure 2 shows the process flow of preparing a homogeneous precursor solution. Barium neodecanoate and sodium 2-ethylhexanoate and niobium ethoxide were selected as starting materials. Xylene, 2-methoxyethanol and 2-ethylhexanoic acid were selected as solvent. Barium neodecanoate dissolved in xylene solvent mixed with 2-methoxyethanol; sodium 2-ethylhexanoate dissolved in 2-ethylhexanoic acid; and niobium ethoxide dissolved in 2-methoxyethanol in an N₂ dry box. The solutions were stirred for two hours at room temperature respectively, then mixed together, and then stirred continuously for three hours at R.T.. The final concentration of the BNN precursor solution was 0.2M. The solution was homogeneous and of light yellow colour.

BNN thin films were prepared by spin-coating at 3000rpm for 30s onto Si or Pt substrates. The preparation process is shown in figure 3. After spin-coating, the films were dried on a hot plate at 350°C for 10 minutes in air and then calcined in a furnace at 650°C for 4 minutes. The coating-baking process was repeated several times in order to increase the film thickness. Crystallization behavior was analyzed by XRD (D/MAX-2500, Rigaku, Japan). Surface morphology and profile of thin films were observed using SEM (S-4100, Hitachi, Japan).

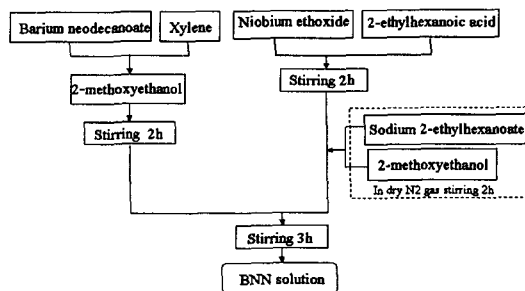


Fig.2. Preparation process for BNN solution

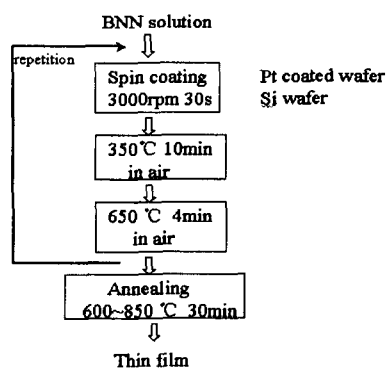


Fig.3. Thin film preparation process

3. Results and Discussion.

Figure 4 shows XRD patterns for stoichiometric Ba₂NaNb₅O₁₅ thin films annealed at different temperatures on Si(100) substrates. The annealing time was 30 minutes. It could be seen that at low annealing temperatures (such as 75 0°C), the signals of tungsten bronze structure were weak. Most of peaks belonged to BaNb₂O₆ phase. However, when temperatures of annealing were increased, the peaks of BaNb₂O₆ decreased, and the signals of TTB structure became strong. At about 1000°C, The BaNb₂O₆ phase disappeared and we got the single TTB phase BNN films. BaNb₂O₆ phase appeared in BNN crystal during the crystallization process, which was also reported in other peoples papers [9,10]. So the BaNb₂O₆ phase should be the metastable phase in stoichiometric BNN film. When the film was heated at a high temperature,

the metastable phase changed into a more stable structure (TTB structure). The higher crystallization temperature of film is considered to be attribute to the complex crystal structure of tungsten bronze. But the temperature of 1000°C is too high for Pt coated wafer.

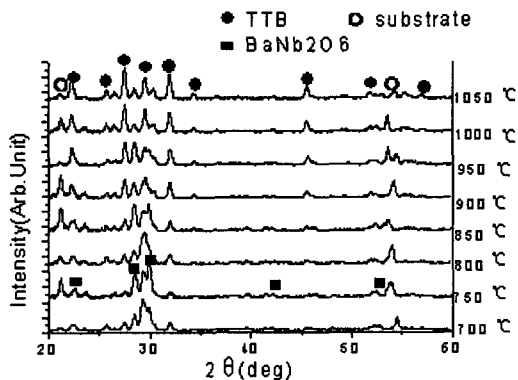


Fig. 4. XRD patterns of $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ thin films annealed at different temperatures on Si(100) substrates.

To study the effects of composition on crystallization behavior of H-MOD derived BNN thin films, BNN thin films with different compositions were prepared. The compositions of films are shown in ternary phase-diagram of $\text{BaO-Na}_2\text{O-Nb}_2\text{O}_5$. (Fig.5). The pentagon indicates the composition of stoichiometric $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$. The diagram (b) is the portion of diagram (a) nearby the stoichiometric composition point.

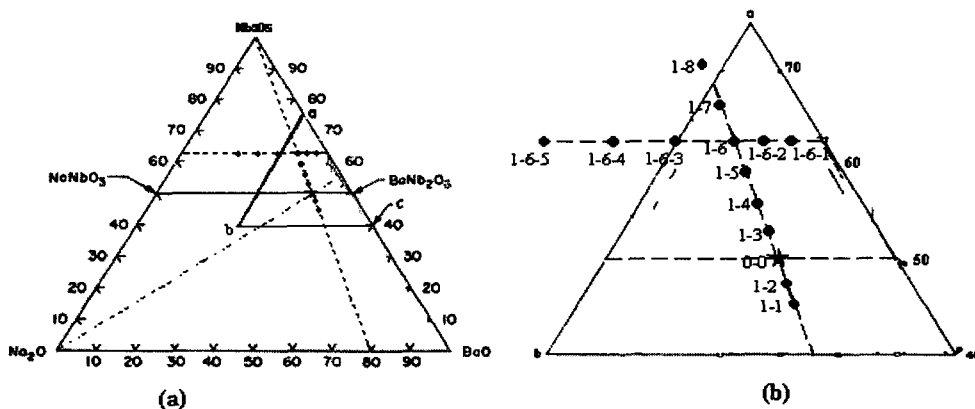


Fig.5. Ternary phase-diagram of $\text{BaO-Na}_2\text{O-Nb}_2\text{O}_5$

Figure 6 shows the XRD patterns of BNN films with different compositions coated on Pt(100) substrates. The composition varies along the line ((1-1) ~ (1-6)) in phase diagram (Fig.5), during which, the ratio of $\text{Ba}^{2+}/\text{Na}^+$ is fixed; however the content of niobium is variational. The annealing condition was fixed at 750°C for 30minutes. The XRD patterns show that film with stoichiometric composition has a mass of unwanted phase. When the Nb_2O_5 content was increased to 62.5% (composition number is 1-6), the unwanted phase disappeared, and we got TTB structure BNN thin film. (In stoichiometric BNN, the Nb_2O_5 content is 50%). The reason why the film needs excess niobium is difficult to explain. As some paper reported previously, if excess niobium was added in BNN crystal, even though at a high temperature (more than 1000°C), the excess niobium ion did not form NbO_6 octahedra but enter into A sites and covalently bonded to the oxygen ions [11]. So in H-MOD process, because of the lower annealing temperature (such as 750°C), it is difficult for all of niobium ions to form NbO_6 octahedra, which caused the deficient of NbO_6 octahedra, so there are no enough A sites for introducing the Ba^{2+} and Na^+ into the lattices. This situation made the formation of tungsten bronze structure in stoichiometric BNN difficult at low temperatures.

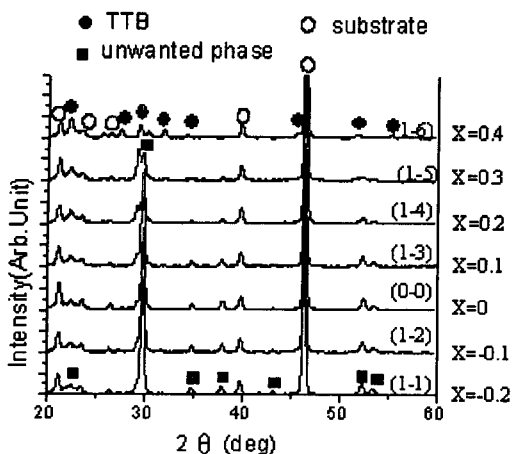


Fig. 6. XRD patterns of $Ba_{2(1-x)}Na_{(1-x)}Nb_5O_{(15-5x/2)}$ thin films with different x values prepared on Pt(100) substrates.

Figure 7 shows the SEM micrographs of BNN films with different compositions (corresponding to the composition number (0-0,1-4,1-6)) in figure 5. From the cross structure photographs we can see the thickness of films are about 5000 Å. The surface photographs show that the BNN film with composition of $Ba_{1.2}Na_{0.6}Nb_5O_{14}$ has a random polycrystalline structure. But in stoichiometric BNN (0-0) film the grain growth direction is parallel the plane of substrate. This can explain that stoichiometric BNN has a very strong peak nearby $2\theta \approx 30^\circ$ in XRD patterns. In photographs of film with composition of $Ba_{1.6}Na_{0.8}Nb_5O_{14.5}$ (composition number is 1-4), part of grains are the same as those in film $Ba_2NaNb_5O_{15}$, and some grains are the same as those in $Ba_{1.2}Na_{0.6}Nb_5O_{14}$. That is because the composition of $Ba_{1.6}Na_{0.8}Nb_5O_{14.5}$ (1-4) is between the composition of the film (0-0) and the composition of film (1-6).

Figure 8 shows the XRD patterns of BNN films with the composition of $Ba_{1.2}Na_{0.6}Nb_5O_{14}$ (1-6) annealed at different temperatures. The result shows the film crystallization started at temperature of about 650°C. Figure 9 shows the SEM micrographs of BNN film corresponding to XRD patterns in figure 8. The surface photographs indicated that the films are crack-free, uniform with small grain size

(0.05–0.12 nm). It is clear that the grain growth started at about 650°C, and at 700°C the grain size had a great increase. These results are corresponding to the XRD results in figure 8. The grain size increased with the increase of annealing temperature.

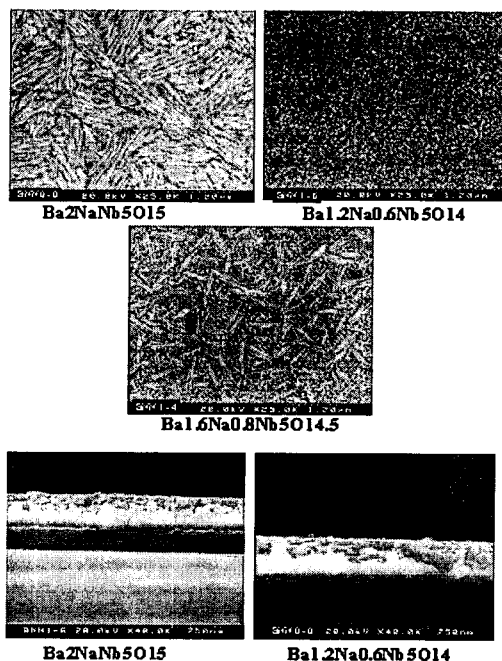


Fig. 7. Plane and cross-sectional SEM micrographs $Ba_{2(1-x)}Na_{(1-x)}Nb_5O_{(15-5x/2)}$ thin films on Pt(100) substrates.

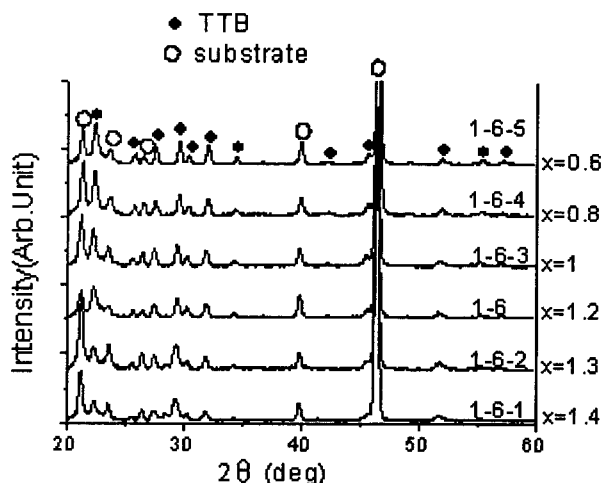


Fig. 8. XRD patterns of $Ba_{1.2}Na_{0.6}Nb_5O_{14}$ thin films annealed at different temperatures.

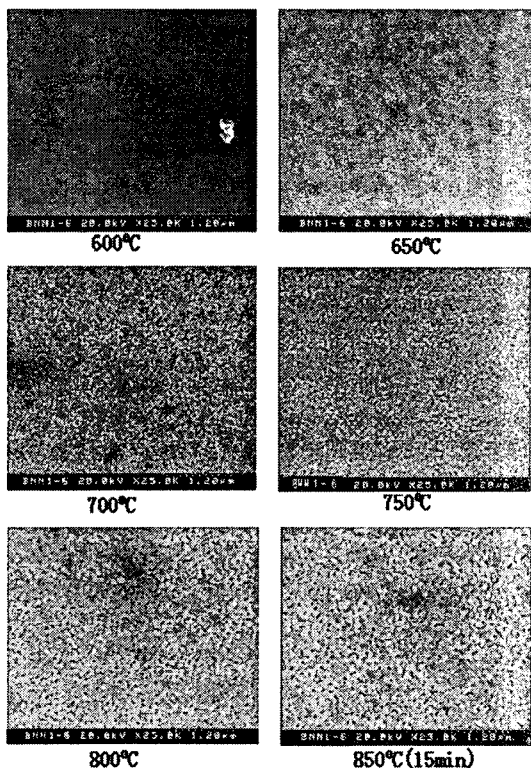


Fig. 9. SEM photographs of $Ba_{1.2}Na_{0.6}Nb_5O_{14}$ thin films annealed at different temperature on Pt(100) substrates.

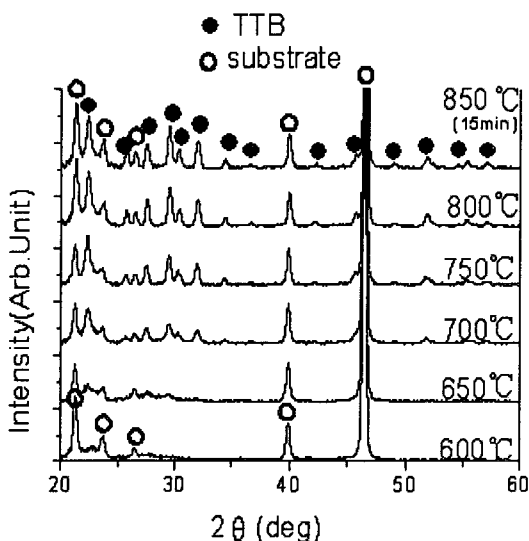


Fig. 10. XRD patterns of $Ba_xNa_{(3-2x)}Nb_5O_{14}$ thin films with different x values on Pt(100) substrates.

The XRD patterns of BNN films with other different composition were prepared (Figure 10). The compositions of films are corresponding to the line ((1-6-1) ~ (1-6-5)) as shown in phase diagram. It indicates that the niobium content is fixed, but the Ba^{2+}/Na^{+} ratio in films is changing. The XRD patterns of these films are similar. This result sustains that the structure of $Ba_{1.2}Na_{0.6}Nb_5O_{14}$ is TTB structure, for in TTB structure Ba^{2+} ions and Na^{+} ions can substitute partially.

4. Conclusion

Crack-free BNN films were synthesized on Si or Pt (100) substrates using a hybrid MOD process. Crystallization behaviors were studied as a function of film composition and annealing temperature. The crystallization started at about 650°C. It was found the niobium content had a marked effect to the formation of TTB structure, the TTB structure appears when the films been added excess niobium.

References

1. S.Singh, D.A. Draeger and J.E. Geusic, *Phys. Rev. B*, 2, 2709-2724(1970)
2. Geusic, J.E., Levinstein, H.J., Rubin, J.J., Singh, S. and Van uniter, L.G., *Appl. Phys.Lett.*, 11,269(1967).
3. Van Uniter, L.G., Rubin, J.J. and Bonner, W.A., *IEEE J. Quantum Electronics*, 4,622(1968).
4. J.S.Abell, K.G.Barracough, I.R.Harris, A.W.Vere and B.Cockayne, *J. Mater. Sci.* 6,1084(1971).
5. P.B.Jamieson *et al.*, *J. Chem. Phys.*, 48,5048(1968).
6. Masuda, Y., Masumoto, H., Kidachi, Y., Watazu, A., Baba, A., Goto, T. and Hirai, T., *Jpn. J. Appl. Phys.*, 34,5124(1995).
7. Yogo, T., Sakamoto, W., Isaji, T., Kikuta, K. and Hirano, S., *J. Am. Ceram. Soc.*, 80,1767(1997).
8. J.S.Wright *et al.*, *J. Electroceramics*, 3(3), 261(1999).
9. Gaku F., Atsushi K., Shizutoshi A., Soichiro O., *J. Ceram. Soc. Jan.*, 105-486(1997).
10. J.M. Boulton, G. Teowee, W.M. Bommersbach and D.R. Uhlmann, *Mat. Rec. Soc. Symp. Proc.*, 243,303(1992).
11. J.R.Carruthers and M.Grasso, *Mat. Res. Bull.* 4. 413-424(1969).